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13. ABSTRACT (Maximum 200 words) Studies of gas adsorption in carbon nanostructures are described. Personnel involved in the project include faculty, students and postdoctoral fellows at Penn State University (Department of Physics) and the University of Pittsburgh (Department of Chemical and Petroleum Engineering). The principal methods employed are analytical or numerical theory and computer simulation. In addition, successful collaborations with experimental scientists (at our institutions and elsewhere) have taken place. A focus of this research is the prediction of the thermodynamic properties of gases adsorbed on nanotubes; also, studies of the spectroscopic properties and momentum distribution of hydrogen have been carried out. In most cases, experimental data on gas adsorption are consistent with these predictions. In some cases, especially hydrogen, the data are particularly dependent on the material preparation and the kind of experimental study of the adsorption. We have developed sophisticated models that improve upon conventional assumptions about the tubes' electronic properties and their consequences for adsorption. We have also investigated consequences for the adsorption of polydisperse tube size distribution and dilation of the tube lattice in a nanotube bundle.				
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Theory of Gas Adsorption in Carbon Nanostructures

ARO #39194-CH; DAAD19-99-1-0167

Final progress report

May 20, 2003

### A.Statement of problem:

The properties of gas adsorbed in various nanotubes are to be studied by state-of-the-art theory and simulation methods and the relation to past and future experiments established.

### B.Summary of results:

Numerous properties of gases adsorbed on the many kinds of nanostructures have been intensively studied during the course of this work. As listed below, 26 research publications, supported by ARO, have been submitted or published by our group during the duration of the support. These articles represent significant contributions to scientific understanding of this field, which remains as a central problem in the fundamental nature of matter, with enormous potential for applications. The research continues, undiminished in intensity, in our laboratories and many others around the world.

One focus of our efforts has been a conceptually simple problem: what are the thermodynamic properties of a particular gas when adsorbed on a particular nanotube structure, in equilibrium with a coexisting vapor phase at a specified pressure and temperature of that gas? We have answered this question in great detail for nearly all inert gases and for a few other simple gases, like hydrogen and methane. The methods used are primarily computer simulation (both classical and quantum), but in some instances theoretical modeling has been employed. In these calculations, our work has usually employed very simple assumptions about the geometry and interactions that are present. It has been rewarding to find that experimental data coming from some laboratories are in good agreement with these calculations. Such data are primarily adsorption isotherms for the simple gases mentioned above. The consistency implies that the simple models are sufficient to characterize this problem *for those gases and experiments*. It must be noted that sample preparation differs between experiments so that many results do *not* agree with our predictions

A major motivator of research in this field, including our own, has been experimental data from a number of laboratories revealing unexpectedly large uptake of hydrogen by various carbon nanostructures. Hydrogen has also been found to be anomalous in other respects; for example, its effect on the thermoelectric power of nanotubes has the opposite sign from that of all other gases which have been studied. We have spent considerable effort exploring the "anomalous" hydrogen problem from a number of theoretical perspectives. A natural starting point is that the molecule is smaller than those of other gases that have been studied. This points, for example, to a possible role of the interstitial region, which is a logical home for a small molecule. Indeed, we found that the hydrogen molecules have sufficient energy incentive to spread the nanotubes apart in order to accommodate them; the effect of this "dilation" is a doubling of the hydrogen binding energy. Also, a many-body calculation in the case of interstitial hydrogen indicates that a more sophisticated pair potential is needed than the usually assumed free space interaction. These calculations suggest a few possible directions for future research. One such direction has just begun- a study of the effect of holes or other impurities in the tubes' walls. At least one practical application has emerged from this research- the use of nanotubes as a molecular sieve for hydrogen isotope and other gas separations.

Our research programs have been closely connected to experimental programs at our universities. This has led to coauthored publications involving thermal desorption experiments, neutron scattering experiments and adsorption isotherm measurements of gas adsorption on carbon nanostructures. We have kept close contact, without formal collaboration, with all of the many other experimental groups that are active in this field.

Our current and near-future work will address some important problems that remain to be investigated. A key question pertains to the effect of the tubes' radius of curvature on its interaction with hydrogen; the necessary analysis involves density functional theory, quantum Monte Carlo and coupled cluster calculations. A related problem to be investigated is the nature of hydrogen adsorption on the intermediate-diameter  $sp^3$  C-H nanotubes, proposed recently by Stojkovic, Zhang and Crespi. Selective removal of hydrogen from the highest-strained sites could produce a tube with mixed  $sp^2/sp^3$  character and strips of semiconductor/metal  $sp^2$  carbon embedded in an insulating  $sp^3$  carbon matrix. Other areas of particular interest in the near term are the dynamical properties of the adsorbate, the effect of a broad distribution of tube sizes in a bundle and the potential development of gas-separation technologies.

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